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Study of composition of the ultrafine material produced from graphite–catalyst mixture under extreme energy action

N V Melnikova[1], D O Alikin[1], Yu B Melnikov[1,2], I G Grigorov[3], S A Chaikovsky[4], N A Labetskaya[4], I M Datsko[4], V I Oreshkin[4,5], N A Ratakhin[4] and K V Khishchenko[6]

[1] Ural Federal University, Lenina Avenue 51, Ekaterinburg 620000, Russia
[2] Ural State University of Economics, 8 Marta Street 62, Ekaterinburg 620219, Russia
[3] Institute of Solid State Chemistry of the Ural Branch of the Russian Academy of Sciences, Pervomaiskaya Street 91, Ekaterinburg 620219, Russia
[4] Institute of High Current Electronics of the Siberian Branch of the Russian Academy of Sciences, Akademichesky Avenue 2/3, Tomsk 634055, Russia
[5] National Research Tomsk Polytechnical University, Lenin Avenue 30, Tomsk 634050, Russia
[6] Joint Institute for High Temperatures of the Russian Academy of Sciences, Izhorskaya 13 Bldg 2, Moscow 125412, Russia

E-mail: nvm.melnikova@gmail.com

Abstract. Ultrafine materials were produced under conditions of extreme energy effects on the mixture of graphite and Ni–Mn catalysts. For the purpose to obtain various forms of carbon, including diamond-like forms, experiments were performed on a MIG high-current generator with the current amplitude of 2–2.5 MA and current rise time of 100 ns. The composition of the explosion products was studied using x-ray diffraction and x-ray phase analyses, the impedance spectroscopy, optical and scanning electron microscopy, x-ray microanalysis and energy dispersive x-ray analysis and the laser confocal Raman microscopy. It was found that the carbon in the studied materials is in the graphite, diamond-like (the faceted particles or agglomerates of faceted particles in size about or less than 250 nm) and amorphous forms.

1. Introduction

Nano-crystalline and ultradispersed structures based on carbon materials are of great interest today. Their unique physical and chemical properties results in lots of applications. The properties of ultradispersed materials depend on their methods of synthesis. The basic methods for production of the ultradispersed carbon materials are (i) synthesis from natural diamonds by physical methods, (ii) synthesis at high pressures and temperatures, (iii) electron and ion beam methods utilizing irradiation of electron beams and argon ions of carbonaceous material, (iv) chemical vapor deposition of containing carbon vapor at high temperatures and pressures, (v) detonation synthesis, (vi) electrophysical methods [1–3]. Electrophysical methods are widely applicable for production of ultradispersed materials [4, 5]. Advantage of these methods is the possibility to realize the conditions required for the synthesis of various carbon phases, in particular of diamond-like forms and lonsdalite (hexagonal diamond), whose strength is higher

than that of diamond by a factor of 1.5 [6]. Lonsdalite is formed at high pressures (P = 30–70 GPa) and temperatures (about 1200 K). These conditions can be realized during electrical explosion using multimegaampere generator [5], which we used in this study. The purpose of this work is studying the composition of ultrafine materials produced under conditions of extreme energy effects during electrical explosion on the mixture of graphite and catalysts, and examining carbon forms including diamond-like forms in resulting materials.

2. Materials and experiment

Experiments on electrical explosion were performed on a MIG high-current generator with the current amplitude of 2–2.5 MA and current rise time of 100 ns (the technical characteristics are described in detail in [5]). In the experiments, the explosion of copper tubes of diameter 4 mm and wall thickness 0.5 mm was studied. The tubes were filled with a mixture of industrial graphite and Ni–Mn catalyst in the ratio of 50/50 wt %; the Ni to Mn ratio was 50/50 wt % as well. This method make it possible to produce ultradispersed carbon materials ranging in size from 1 to 1000 nm. The samples were obtained by precipitation of the electrical explosion products on glass substrates placed 5–50 cm away from the exploded load. In the present work, three samples (1, 2 and 3) placed 41–42 cm away from the exploded load, were studied. The substrate for sample 1 was placed perpendicular to the main direction of dispersion of the particles and substrates for samples 2 and 3 were placed under angles about 10° to main direction of dispersion. The samples were studied using x-ray diffraction and x-ray phase analyses (Stadi-P, Stoe), the impedance spectroscopy (Solartron 1260A and ModuLab MTS), optical microscopy (METAM RV-34 and Carl Zeiss), scanning electron microscopy, x-ray microanalysis and energy dispersive x-ray analysis (JEOL–JSM 6390 LA, USA and Auriga CrossBeam, Carl Zeiss), and the laser confocal Raman microscopy (Alpha300 R, Witec).

3. Results and discussion

Optical images of the samples are presented in figure 1. The largest particles, including not evaporated pieces of metals, wires (figure 1a–c) etc, were observed in samples 1 and 2—in the films deposited on the substrate closest to the load (figure 1). In sample 3 with thinner layer of the film on the substrate, smaller particles dominated.

According to x-ray diffraction and x-ray phase analyses, copper (space group number 225, space group symbol $Fm\bar{3}m$, lattice parameter a = 0.36187 nm) and possibly the crystalline materials such as nickel and diamond with a cubic structure similar to the copper crystal structure occupied about 93% of the area of sample 1, and carbon in the form of a graphite (space group number 194, space group symbol $P6_3/mmc$, lattice parameters a = 0.24640 nm, c = 0.66987 nm, $\gamma = 120°$)—about 7%. The brilliant particles of copper and other metals occupied about 5% of the area of samples 2 and 3, and carbon in the form of graphite—about 10%. To confirm the presence of metallic particles, in particular of copper, we used resistivity measurements by the method of impedance spectroscopy [7]. The impedance technique is one of the extensively used approaches for studying the electrical properties of heterogeneous materials, which allows the contributions associated with electrical conduction of different phases, interfaces, electrode processes, electric polarization, measuring cell *etc* to be distinguished from the material's response to the external electric field. Using the impedance spectroscopy method to the study of the electrical conductivity and resistivity of the films [8], we found that the film containing the largest particles (sample 1) has low electrical resistance ($\approx$ 500 Ohm), and the hodograph of the impedance is typical for the active resistance (figure 2, inset). Such low electrical resistance of the film is caused by presence of a large number of unmelted particles or molten and evaporated and then accordingly solidified or condensed metal particles such as copper, iron, nickel, which form substantially the continuous conductive matrix. Therefore, the non-conductive crystalline forms of carbon, such as diamond-like particles, can

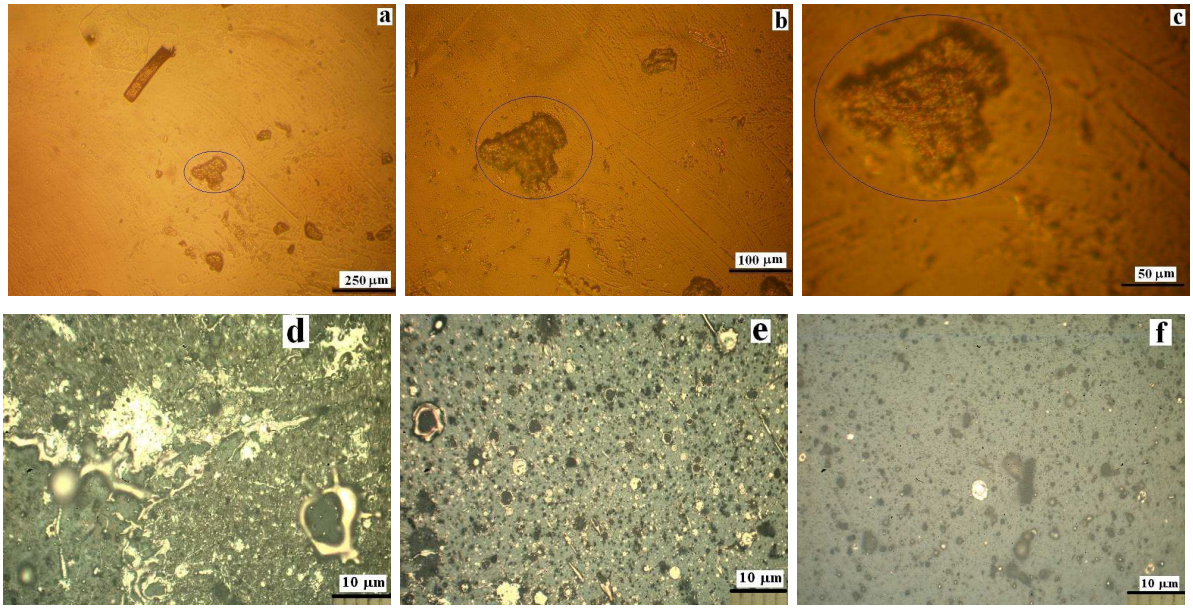

Figure 1. Optical images of sample 2 (a–c) as well as samples 1, 2 and 3 (d, e, f, respectively).

probably be found not on the glass substrate but on the surface of the particles solidifying upon cooling. For samples 2 and 3, which are films with smaller particles, the impedance spectra are practical vertical straight lines (figure 2). This type of impedance hodographs is typical for cells with dielectric samples and corresponds to the equivalent circuit representing the series connected resistor and capacitor (figure 2). The impedance $Z = \mathrm{Re}Z + i\mathrm{Im}Z$ of a circuit that represents serially connected resistance R_0 and capacitance C is determined by following relations:

$$\mathrm{Re}Z = R_0, \tag{1}$$

$$\mathrm{Im}Z = -(\omega C)^{-1}, \tag{2}$$

where $\omega = 2\pi f$ is the angular frequency, f is the linear electric field frequency. Equations (1) and (2) define parametrically a vertical line in a plane $\mathrm{Re}Z$, $-\mathrm{Im}Z$ (figure 2). Resistor and capacitor simulate respectively the ohmic resistance of the particles in the film and the effective capacitance, which is determined by capacitances of capacitors connected in series, each of those is formed by conductive areas bounded by non-conductive borders. Ultrafine crystalline carbon materials, in particular, diamond-like particles, in samples 2 and 3 can be located on the glass substrate and also on the surface of larger particles.

For characterization of the particles in the films, the scanning electron microscopy and energy-dispersive analysis (EDS) were used. Excited volume in EDS method for the accelerating voltage 20 keV is about 1 μm. In our case, where particle thickness was about 100–250 nm, we have registered additional signal from the substrate. Therefore, we have measured 200 nm size particles at the surface of big one with diameter about 3.5 μm (figure 3). It was expected that these small particles are diamond-like. Because a solubility of graphite in the molten metal is higher than a negligible solubility of the diamond (a diamond solubility in molten metals has been studied in [9]), so a metal solution, unsaturated by graphite, will be supersaturated by diamond. The diamond will transform to the solid phase from the bulk on the surface of the metal particles, which evaporate during the electrical explosion and then condense. The data of EDS, analysis of the maps of the element distribution and the profile along a predetermined line,

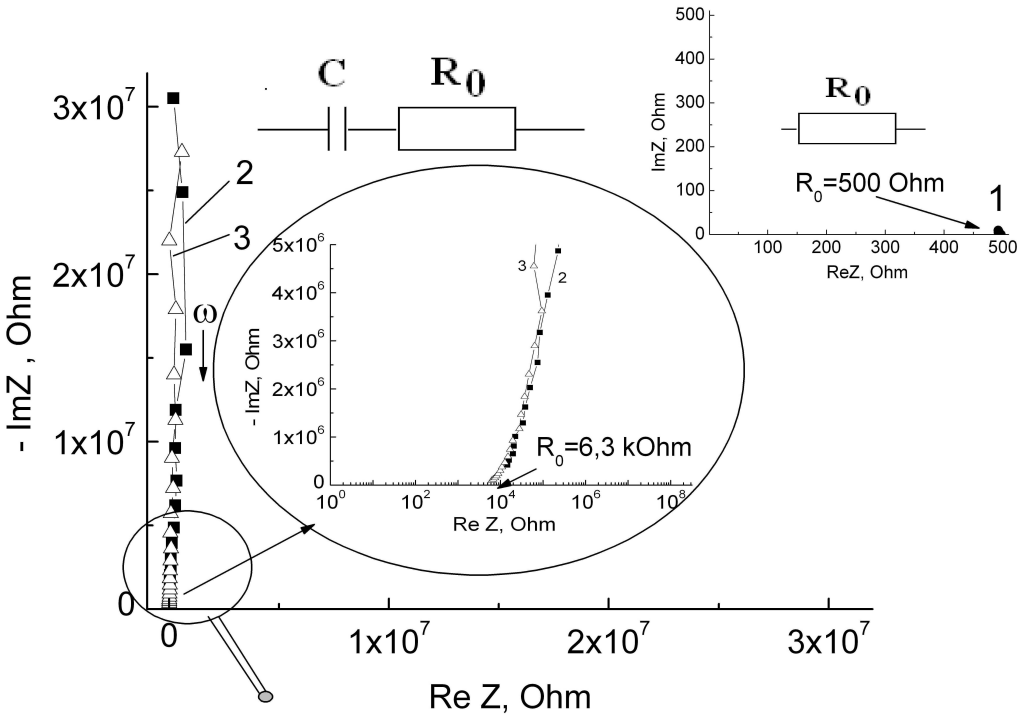

Figure 2. The experimental impedance hodographs of samples 1, 2, 3 (corresponding numbers are presented near the hodographs) and the equivalent circuits.

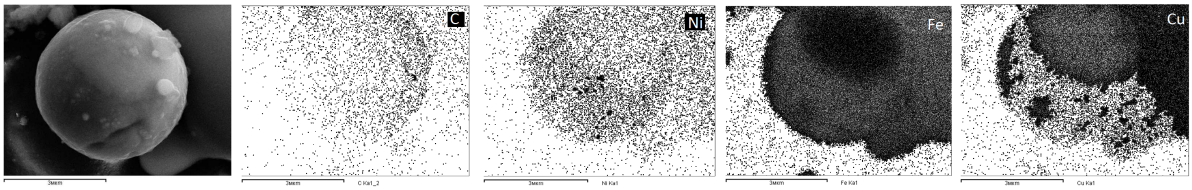

Figure 3. SEM images of sample 1 (from the left-hand side) and EDS maps: C $K_{\alpha 1,2}$, Ni $K_{\alpha 1}$, Fe $K_{\alpha 1}$, Cu $K_{\alpha 1}$.

allowed revealing that spherical particles composed mainly of carbon, iron, copper and nickel. The carbon atoms are of 33%.

To detect and characterize forms of carbon, aside from graphite (the presence of which has been determined by several methods), further studies the particles of size $\approx$ 200 nm or smaller were carried out. The faceted particles or agglomerates of faceted particles in studied materials were found. SEM images of sample 3 are presented in figure 4. We suggest that these faceted particles are carbon or copper particles. Energy-dispersive analysis, analysis inside the area containing particles is demonstrated existence of the carbon, which can be a sign that faceted particles are the diamond-like phase of carbon.

The method based on the laser confocal microscopy and Raman spectroscopy (Raman confocal microscopy) was applied to investigate film structure and to confirm the presence of diamond-like carbon particles in the samples. Raman spectroscopy is widely used for characterization of carbon nanomaterials [10]. Raman spectroscopy is the most sensitive to highly symmetric covalent bonds with small or missing dipole moment. The carbon–carbon bonds completely meet this criterion, so Raman spectroscopy is capable discerning small changes

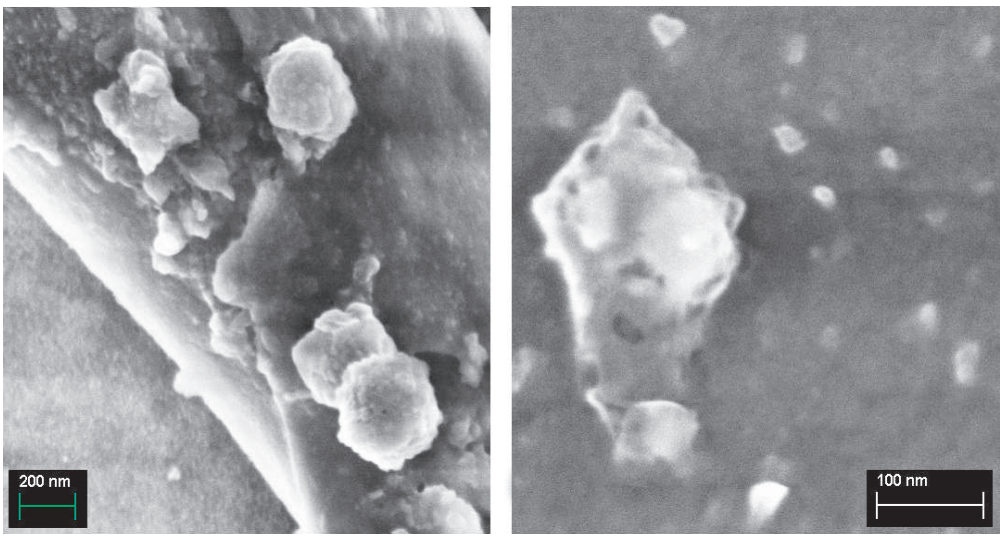

Figure 4. Images of the faceted nanoparticles obtained by SEM micrographs in sample 3.

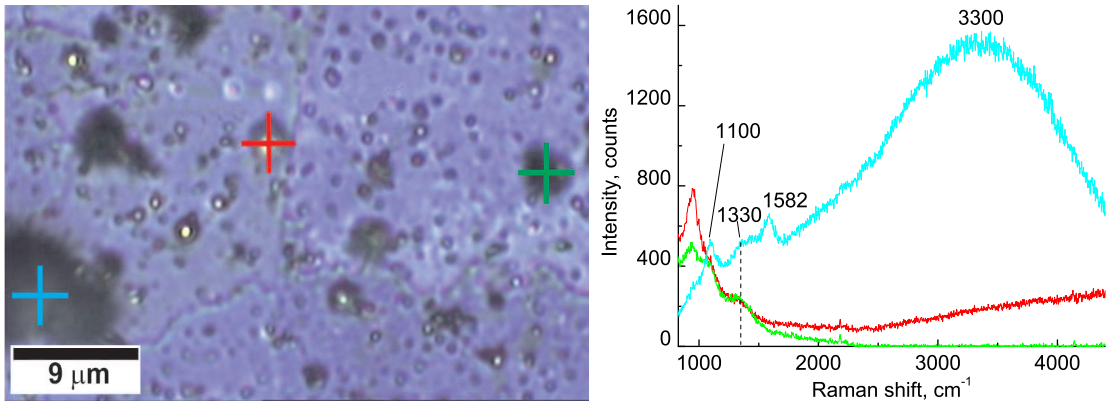

Figure 5. The surface and Raman spectra of sample 3 (the color of the curves corresponds to the color of the crosses) by confocal Raman microscope Alpha 300 R. The diode-pumped solid state laser with $\lambda = 488$ nm was used as a pumping source.

in the structure of the material, making it a very valuable method for the investigation of carbon ultradispersed structures. Confocal Raman microscopy allows realizing mapping of the sample surface with registration of Raman spectra in each point of the map. Further, we can analyze spectra and extract images with area, width, shift of the bands or other parameters. Confocal principle helps to reduce noise caused by light, which achieve CCD detector out of focus plane. The contrast of resulted images becomes higher and spatial resolution increase to the values about 200–300 nm lateral and 0.5 μm depth. Due to limited depth resolution the Raman spectra of the very thin film deposited on a glass substrate will represent a superposition of spectra of the film and the substrate material. In the case of sample 1, with large metal particles, superposition of luminescence (from the metal particles) and the Raman spectrum was observed. On the Raman spectra of sample 2, the intensity maximum at Raman shift ≈ 1100 cm^{-1} correspond to the strongest reflection from the glass substrate (SiO_2).

The surface and Raman spectra of sample 3 are presented in figure 5. On the light blue curve corresponding to the region, marked with a light blue cross, the lines are observed at ≈ 1100,

≈ 1330 and 1582 cm^{-1}, and when the Raman shift > 1700 cm^{-1} a broad halo is observed. The band ≈ 1100 cm^{-1} corresponds to the strongest line of the Raman spectrum of the substrate, the bands ≈ 1330 and 1582 cm^{-1} appear due to the presence of carbon in the forms of diamond (1332 cm^{-1} is diamond band [10]) and graphite (the 1582 cm^{-1} band of graphite is known as the G band [9]) respectively. The halo can be attributed both to the luminescence of the metal particles and to the bands associated with conjugated bonds in the amorphous carbon [10]. In the areas marked by red and green crosses the bands ≈ 950 cm^{-1} can correspond to line of the Raman spectrum of the substrate. The line near 1330 cm^{-1} can be assigned to the D band of graphite or to the diamond form of carbon. Absence of the G band of graphite 1582 cm^{-1} in Raman spectra confirms that not graphite forms of carbon but diamond-like particles can be in these areas of the films. The broad band with the width ≈ 328 cm^{-1} and with the position of the maximum at ≈ 1340 cm^{-1}, estimated by unfolding the spectra into Gaussian components, can be attributed to the presence of nanocrystalline diamond or ultrafine diamond-like particles [10]. Presence of the relatively weak lines corresponding to the diamond or diamond-like forms of carbon [10] leads to the conclusion that the ultrafine diamond-like particles have a size smaller than the resolution of confocal Raman microscope, i.e. about or less than 200 nm and their concentration is too small to give significant input in spectra from laser spot.

Thus, the carbon in the studied materials is detected in the forms of a graphite, diamond-like carbon (the faceted particles or agglomerates of faceted particles of size about or less than 250 nm) and amorphous carbon. To specify the parameters of the crystal structure of the carbon forms and to determine the features of the electronic structure it is necessary to use other techniques, in particular the transmission electron microscopy that allowed the authors [5] to determine the parameters of the crystal modifications of carbon, and the method of ultrasoft x-ray emission spectroscopy [11].

4. Conclusions

Study of composition of the ultrafine materials produced under conditions of extreme energy effects on the mixture of graphite and catalysts were carried out. The analysis of experimental data made it possible to estimate the presence in the samples of three main fractions: chaotic coarse agglomerates with an average size of a few tens of microns, spherical particles of size from hundreds of nanometers to several microns, and faceted particles and fine grains (of size 5–250 nm), that are observed in the samples, including on the surface of the spherical particles. The first fraction is fragment particles, residual metal particles that escaped evaporation in the explosion, and graphite. The second and the third fractions are particles formed due to condensation of the evaporated matter and forming a weakly-conductive (with the resistivity of $\sim 10^7$ Ohm m) film. Carbon in the studied materials is in the forms of (i) graphite, (ii) amorphous carbon and (iii) diamond-like (the faceted particles or agglomerates of faceted particles in size about or less than 250 nm). To determine the parameters of the crystal structure and the features of the electronic structure of the diamond-like forms it is necessary to use the transmission electron microscopy and the ultrasoft x-ray emission spectroscopy.

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